Diode Laser Measurements of HF Concentrations Produced From Heptane/Air Pan Fires Extinguished by FE-36, FM-200, FE-36 Plus APP, and FM-200 Plus APP

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Abstract

Tunable diode laser absorption spectroscopy (TDLAS) is used to measure the time evolution of hydrogen fluoride (HF) concentrations produced from a series of enclosed heptane/air pan fires extinguished by FE-36, FM-200, FE-36 plus ammonium polyphosphate (APP), and FM-200 plus APP. For the fires studied, the change in HF gas concentration with time is dependent upon the fire-fighting chemical used to extinguish the fire. The presence of APP is observed to reduce HF concentrations in the fire enclosure. Visible attenuation spectroscopy is also used to measure the amount of light attenuation (obscuration) that occurs as a hand-held fire extinguisher containing powder fire-fighting agent is released in the crew space of an M1-Abrams land combat vehicle.

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1. Introduction

Fire protection on military platforms, including ground fighting vehicles, is being challenged by the impending loss of the ubiquitous fire-fighting agent Halon 1301 (CF_3Br) due to environmental concerns related to the destruction of the stratospheric ozone layer. Replacement fire-extinguishment agents need to be found that will satisfy numerous criteria including fast fire suppression, minimum production of toxic gases when used, low toxicity, compatibility with storage materials, and environmental friendliness.

The U.S. Army's search for Halon replacement agents has largely involved an empirical approach of testing and evaluation of commercially available compounds/systems. Testing and evaluation of two candidate Halon replacement agents, FE-36 ($C_3F_6H_2$) and FM-200 (C_3F_7H) are presented here from full-scale fire-suppression tests conducted at the U.S. Army Aberdeen Test Center (ATC). The fluorinated propane agents, though effective at extinguishing fires, are deficient in terms of increased weight and volume requirements needed for fighting the most difficult military fires. The increased amounts of replacement agent required for extinguishment, relative to Halons 1301 and 1211, pose a concern with the levels of HF formed as the primary decomposition product. Thus, the tests presented here measure the concentration of gas-phase hydrogen fluoride (HF) using near-infrared (NIR) tunable diode laser absorption spectroscopy (TDLAS) [1]. A recent article from this laboratory details the use of NIR-TDLAS as the most effective diagnostic for gas-phase HF measurements [2].

The two mechanisms by which HF concentrations can be decreased during and following fire-extinguishment by FE-36 or FM-200 are by (1) reducing the time required to extinguish the fire, thereby minimizing the time that the fluorine-containing suppressant is exposed to flame temperatures, or (2) releasing a scavenging agent in conjunction with the fire-suppressant chemical to remove HF after it is produced. A potential chemical scavenging agent of gaseous HF is ammonium polyphosphate (APP), which is a commercially available chemical (Phos-chek)

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with fire-retardant properties. One of the drawbacks to the release of a powder agent in an occupied space is the possibility of reduced visibility.

HF is produced from a series of enclosed heptane/air pan fires extinguished by FE-36 ($C_3F_6H_2$), FM-200 (C_3F_7H), FE-36 plus APP, or FM-200 plus APP. By measuring how much the HF concentrations are reduced in fires extinguished with FE-36 plus APP or FM-200 plus APP mixtures compared to fires extinguished by FE-36 or FM-200 alone, the effectiveness of APP as an HF reduction and potential scavenging agent is demonstrated. In addition, spectroscopic measurements of the amount of light attenuation (obscuration) that occurs as a hand-held fire extinguisher containing powder fire-fighting agent is released in the crew space of an M1 land combat vehicle is discussed.

2. Experimental

Figure 1 shows a schematic diagram of the test facility containing the NIR-TDLAS experimental apparatus and signal-processing electronics. TDLAS has proven to be a valuable nonintrusive optical diagnostic for species concentrations and temperatures in combustion systems, even when the local soot level is high [3–9]. The test facility is a 1.5 m^3 cubic enclosure, which contains a liquid heptane pan fire (fire size approximately 30 kW). The fire suppressants used were FE-36 or FM-200. For the extinguishers with APP added, the following combinations of FE-36 plus APP and FM-200 plus APP were tested: FE-36 plus 7% APP, FE-36 plus 15% APP, and FM-200 plus 15% APP.

The test protocol was as follows: a 250-ml pan filled with heptane fuel was placed underneath a 0.5-m-high steel table within the cubic container. The NIR-TDLAS HF gas measurement apparatus was situated on top of the metal table, where a calibration cell was placed in the line-of-sight path between the gradient index (GRIN) lens from which the 1.3-μm laser radiation was emitted and the InGaAs detector. The calibration cell was used to provide an

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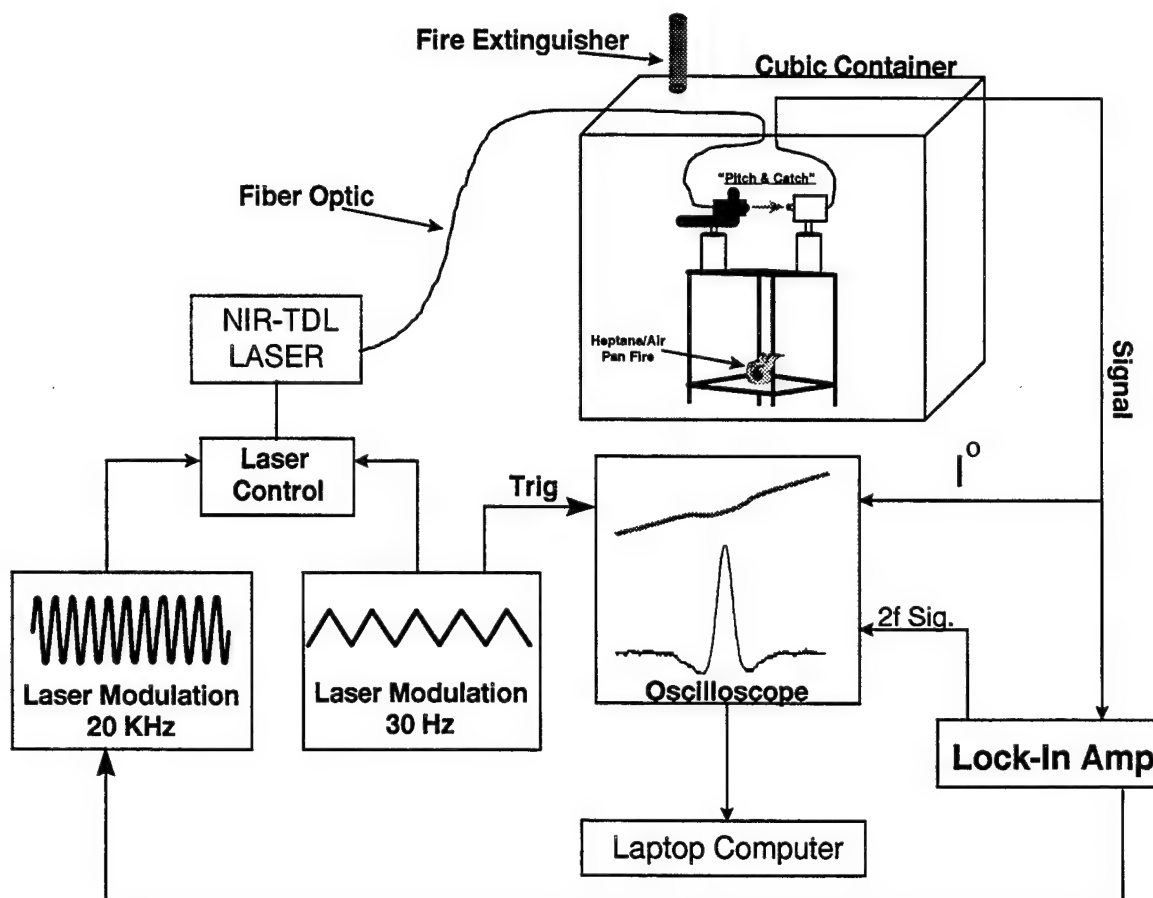
Figure 1. Schematic Diagram of Experimental HF Measurement Apparatus.

HF spectrum to tune the laser and data collection system. The calibration cell was removed prior to fire testing. A hand-held bottle-type extinguisher charged with 770 g of FE-36 plus scavenging agent (when applicable) and pressurized with N_2 gas was situated on top of the cubic container. The extinguisher bottle output nozzle was attached via tubing to a spray nozzle protruding into the cubic container.

The heptane pan fire was ignited using a butane electric match, and the NIR-TDLAS HF gas measurement was initiated immediately after an internal cubic container fan was turned on and the container door was closed. The heptane pan fire was allowed to burn for 15 s at which time the hand-held extinguisher's contents were discharged into the interior of cubic container,

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producing total flooding inhibitor conditions (10% by volume FE-36 concentration). A video camera mounted within the cubic container recorded the fire event during the tests. HF data collection occurred for 180 s after ignition of the fuel at a rate of 1 spectrum per second.

Following each test, the interior of the cubic container was rinsed with an aqueous solution of sodium bicarbonate to neutralize any acid residues on the interior surface and the container was allowed to air dry. The experimental details and analysis of NIR-TDLAS HF spectra have been described previously [2] are only summarized here.

A sawtooth modulation ($\approx$100 Hz) supplied from a Function Generator (Tektronix Model FG 504) was used to rapidly scan over the desired spectral frequency range. Coincident with the 100-Hz modulation was a small-amplitude but higher frequency modulation, $\approx$20 kHz, taken from the sine output of a Stanford Research Systems (SRS) Model 830 DSP lock-in amplifier. The application of the two modulations to the laser diode current facilitated wavelength modulation spectroscopy (2f detection) that was needed for enhanced signal sensitivity [10–14]. Wavelength modulation spectroscopy is convenient for analysis because of the linear relationship that exists between the measured absorption signal and the analyte's concentration. Concentrations of HF were calibrated using a continuous flow cell containing various known mixtures of HF in N_2 and measuring each mixture's unique absorption spectrum.

The emitted infrared (IR) light from the diode was launched into a fiber coupled to the laser housing. Fiber-optic patch cables were used to deliver (IR) light into the test facility. The fiber was terminated by a GRIN lens (Sentech Systems, Inc.), which collimates the laser radiation. The GRIN lens-tipped fiber was placed into a "pitch and catch" arrangement, which directs the (IR) radiation over a 14-cm open path to a InGaAs detector (Epitaxx Model ETX 1000 T). The signal observed at the detector was directed to a phase-sensitive lock-in amplifier (SRS Model 830), which acquired the 2f absorption signal. The 2f output signal from the SRS lock-in amplifier was then sent to a digital oscilloscope (LeCroy Model 9654). Resulting spectra were acquired every second for a 3-min time period and then sent to a Pentium-based laptop computer

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for storage and analysis. For experiments described here, the P(2) transition of the first vibrational overtone of HF was monitored at $7,665 \text{ cm}^{-1}$ [5].

Figure 2 presents a schematic representation of the experimental apparatus used for attenuation testing. The apparatus consists of a HeNe laser (Oriel Model 6611, output 632 nm), an Optical Chopper (SRS Model SR540), and a fiber-optic fiber coupler (Newport Optics Model F-916T). The experimental equipment was mounted to a 46- $\times$ 46-cm optical breadboard, which was placed outside the crew compartment on top of the vehicle. A separate 41-cm optical rail supported the fiber collimating/projection optics and a 15-mm^2 (active element) photodetector (Centro Vision Inc. OSD5-5T, 350-1100 nm). The optical rail was placed inside the vehicle in the driver's seat. Not shown is a plastic enclosure that was placed over the fiber collimating/projection optics to minimize the optic devices from exposure to the powder agent. A 18-m BNC cable and extension cord provided remote signal communications and power to the chopper and laser, while another 18-m BNC cable transported the detector signal out to the detection electronics. The tests consisted of an occupant releasing a Kidde 2.75-lb hand-held fire extinguisher containing either FE-36 plus APP or $NaHCO_3$ plus N_2 at the personnel heater, while inside the vehicle, and all outside hatches were closed. With the hatch doors closed, the vehicle's nuclear and biological containment (NBC) system was operated to create a positive pressure inside the crew compartment.

Light attenuation is determined by monitoring the percent transmission of HeNe laser radiation that is incident on the detector as chemical agent is dispersed over the measurement region. Thus, if 100% transmission occurs, all the light that exits the laser source is incident upon the detector and no attenuation occurred. The laser radiation is passed through an optical chopper, which modulates the laser radiation at $\approx$1,000 Hz. After passing through the chopper, the laser radiation is launched into an 8-m-long visible fiber-optic cable (3M multimode 1,000-mm-diameter core glass-substrate optical fiber). Light passes out the opposite end of the fiber where it is terminated into an 11-mm SMA fiber ferrule (Oriel Model 77670). The
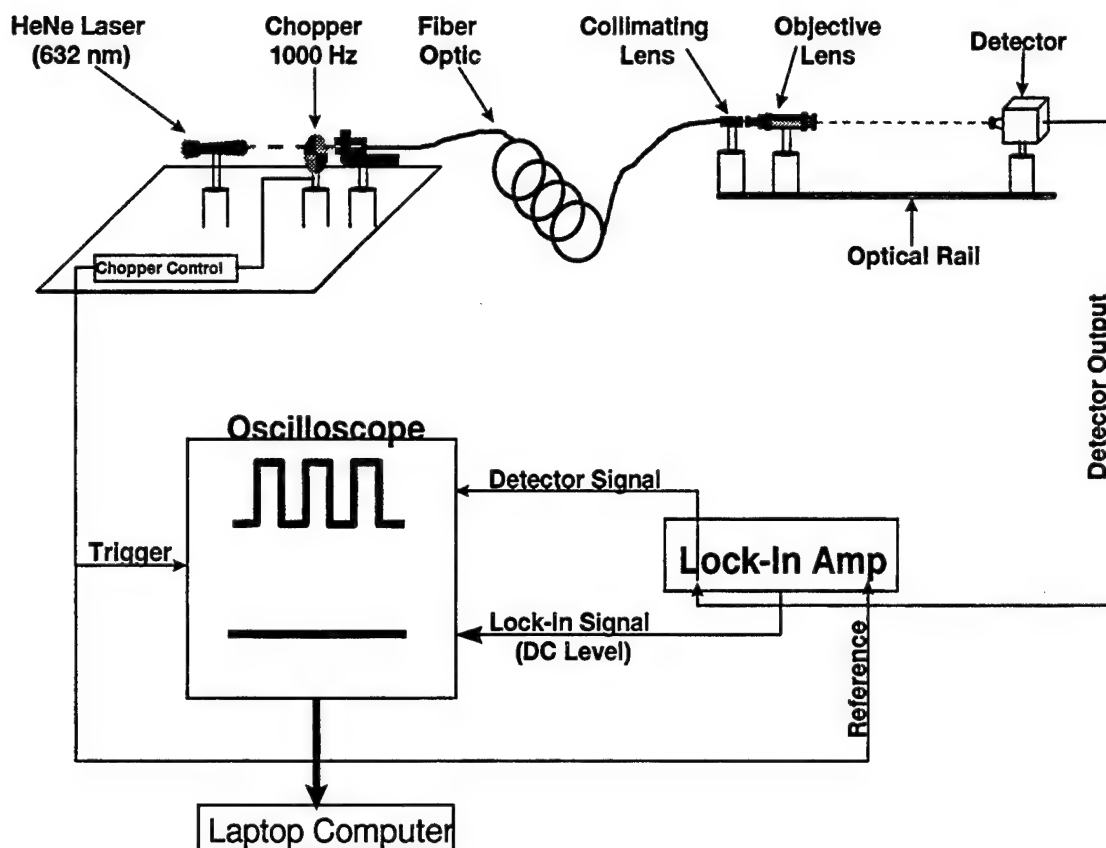
Figure 2. Schematic Diagram of Light Attenuation Measurement Apparatus.

terminated fiber is inserted into a glass-collimating beam probe (Oriel Model 77645). The collimated light exits the beam probe and is directed into a visible Nikon objective lens, which apertures the beam to approximately 5–6 mm and directs it over a 0.4-m free space, where the laser radiation is incident onto the 15-mm^2 photodetector. The free space through which the laser radiation passes is the region in which the powdered agent, if present, will attenuate the laser radiation. The light intensity reaching the detector is converted to a voltage, which is then measured using a lock-in amplifier referenced to the chopper frequency. A direct-current (DC) voltage (0–5-V full scale), proportional to the detector signal, is output to the digital oscilloscope (LeCroy Model 9654), which is also triggered by the optical chopper, and is processed and recorded using a Pentium-based laptop computer at a rate of 2 Hz.

3. Results

Figure 3 presents average HF concentration profiles from extinguishment tests with FE-36, FE-36 plus 7% APP, FE-36 plus 15% APP, FM-200, and FM-200 plus 15% APP. For the FE-36 plus 7% APP and FE-36 plus 15% APP tests, three individual profiles for each extinguisher concentration were used to construct each test's average profile. For the FE-36 profile, test data from five different profiles, collected over the entire testing period, compose the average profile. The FM-200-only average profile is constructed from 10 separate tests, while the FM-200 plus 15% APP profile consists of four separate tests. Statistically the 1-σ variances for the profiles were 41, 42, 31, 56, and 54% for FE-36, FE-36 plus 7% APP, FE-36 plus 15% APP, FM-200, and FM-200 plus 15% APP. For the FM-200 and FM-200 plus APP tests, the large statistical deviations are attributed to inconsistent fire-extinguishment times (explained in more detail next) from test to test, which was not as evident in the FE-36 tests. Table 1 lists the maximum HF concentrations and time-weighted averages from each profile in Figure 3. The results from Figure 3 and Table 1 indicate that fires extinguished by FM-200 produce almost twice as much HF as fires extinguished by FE-36. For fires extinguished by FE-36 plus APP or FM-200 plus APP, the data show that HF is reduced with respect to fires extinguished by the neat agents alone. Table 1 also lists the time-weighted average HF values that represent the average dose of HF one would be exposed to from the time of extinguisher release at $t = 15$ s until the end of the measurement period at $t = 180$ s. The time-weighted average is very important because the primary toxicity concern for HF exposure is not the maximum HF one experiences but the average concentration one is exposed to over a period of time. It should be noted that the target nontoxic HF time-weighted average level for these tests was 500 ppm or less. From Table 1, the HF time-weighted average values imply that, for the tests with FE-36, FM-200, and FM-200 plus 15% APP, the HF dose is toxic, while the tests with FE-36 plus 7% APP and FE-36 plus 15% APP achieve minimum to very acceptable HF reductions, respectively.

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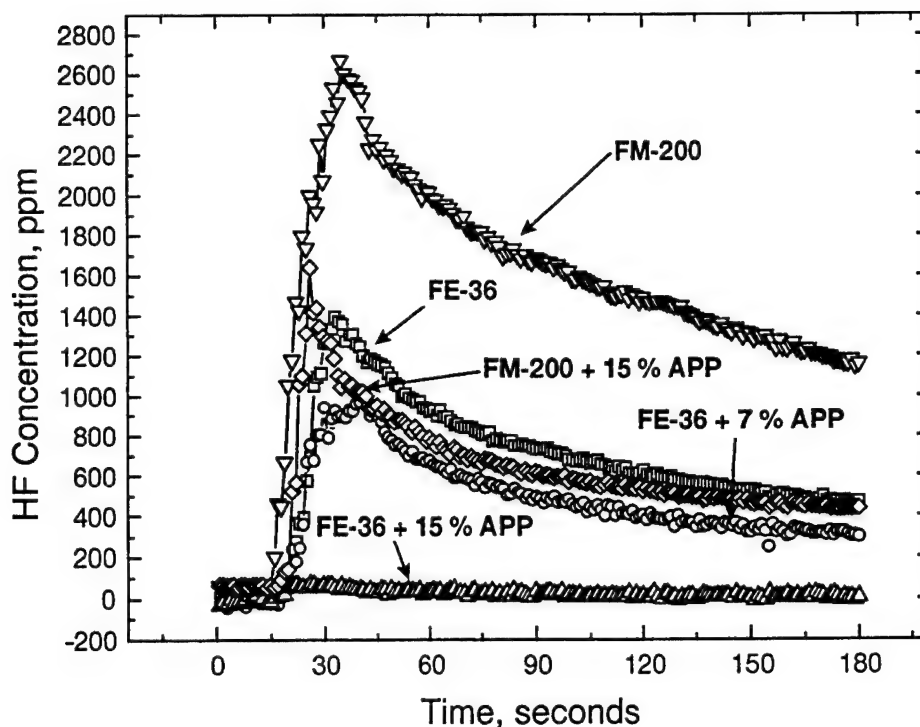
Figure 3. Average HF Concentration Profiles vs. Measurement Time. The (□) Symbols Are HF Concentrations From Fires Extinguished by FE-36, the (○) Symbols Are HF Concentrations From Fires Extinguished by FE-36 Plus 7% APP, the (△) Symbols (Bottom Trace) Are HF Concentrations From Fires Extinguished by FE-36 Plus 15% APP, the (▽) Symbols Are HF Concentrations From Fires Extinguished by FM-200, and the (◇) Symbols Are HF Concentrations From Fires Extinguished by FM-200 Plus 15% APP.

Table 1. Maximum HF Concentrations and Time-Weighted Average HF Concentrations

HF Concentration	FE-36	FE-36 Plus 7% APP	FE-36 Plus 15% APP	FM-200	FM-200 Plus 15% APP
Maximum (ppm)	1,394	996	73	2,667	1,638
Time-Weighted Average (ppm)	712	493	23	1,626	646

Measurement of HF gas concentration vs. time provides a monitor of the fire history and the effectiveness of any HF reduction agent used. That is, the time from fire-suppressant release until the maximum HF concentration occurs is a measure of the time required for fire extinction

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(also verified visually using a video recorder), while the rate at which the HF concentration decreases following extinguishment provides a measure of the effectiveness of scavenging agent (when used) or a measure of the rate at which HF gas reacts with the walls of the enclosure. Reduction in fire out times reduces HF levels by reducing the time the agent is exposed to flame temperatures, which causes agent decomposition to HF. Table 2 lists the fire out times from Figure 3.

Table 2. Fire Out Times From Average Profiles in Figure 3

	FE-36	FE-36 Plus 7% APP	FE-36 Plus 15% APP	FM-200	FM-200 Plus 15% APP
Fire Out Times (s)	18	20	12	20	12

Statistically the difference in fire out times between fires extinguished by FE-36 and FE-36 plus 7% APP are insignificant with a 1-σ error of 22%. For fires extinguished by FE-36 plus 15% APP and FM-200 plus 15% APP, the fire out times were reduced by approximately 33 to 40% relative to the fires extinguished by the respective neat agents themselves. The decrease in the time-weighted average HF levels in Table 1 for fires extinguished using FE-36 and FM-200 compared to fires extinguished by FE-36 plus 15% APP and FM-200 plus 15% APP (approximately a factor of 30 and 2.5, respectively) is partially attributable to the fire-suppression properties of APP (reflected by the shorter fire out times).

Figure 3 and Table 1 indicate that the presence of APP, regardless of the percentage in the extinguisher, helps reduce the overall HF levels with respect to those fires extinguished by only neat agents. A possible explanation for the HF reductions is that, without APP in the enclosure, fires extinguished by the neat agents are able to produce HF more rapidly than fires extinguished by neat agents plus APP. This statement is supported by Figure 4, which plots HF concentrations for each extinguisher from $t = 16$ s to $t = 31$ s, which are the time locations from the extinguisher release to just before the HF concentrations reach their respective maximums in Figure 3. Linear regression analysis of this data indicates that FM-200 produces HF 39% faster than FE-36. For

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the fires extinguished by FE-36, HF is formed 21% faster than the fires extinguished by FE-36 plus 7% APP, while fires extinguished by FM-200 form HF 12% quicker than those fires extinguished by FM-200 plus 15% APP. Obviously, the data in Figure 4 are dependent on the fire out times, and previous studies [15] have shown that, as the fire out times increase this is accompanied by an increase, in the amount of HF present in the system.
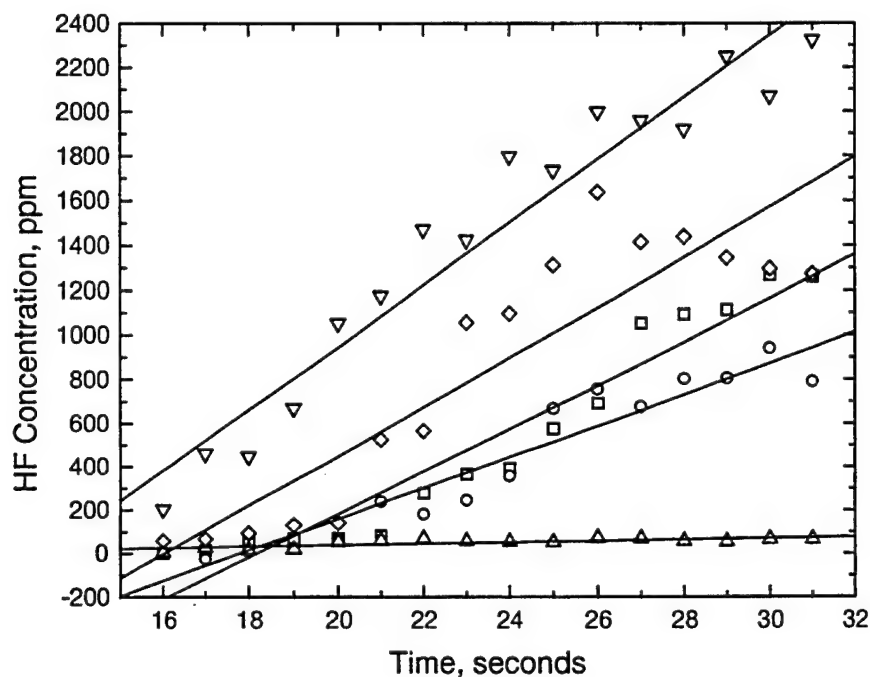
Figure 4. Plot of HF Concentrations vs. Measurement Time From t = 16 s to t = 31 s to Illustrate HF Production Rates. The (□) Symbols Are HF Concentrations From Fires Extinguished by FE-36, the (○) Symbols Are HF Concentrations From Fires Extinguished by FE-36 Plus 7% APP, the (△) Symbols Are HF Concentrations From Fires Extinguished by FE-36 Plus 15% APP, the (▽) Symbols Are HF Concentrations From Fires Extinguished by FM-200, and the (◇) Symbols Are HF Concentrations From Fires Extinguished by FM-200 Plus 15% APP. The Straight Solid Lines Represent Linear Regression Analysis of the Data.

In real fires, reduction of fire out times is difficult to control and, if the time duration is extended, some measures must be taken to control the HF levels. APP is added to these extinguishers because it is believed that APP can heterogeneously scavenge HF from the

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post-flame gases of a fire situation extinguished by a fluorinated fire-fighting agent. To evaluate APP's scavenging abilities, the time rate of change of the HF concentration must be measured.

The rate of change in HF concentration can be compared between extinguishers with and without APP using data from Figure 3, starting at the maximum HF concentration time (t_o) and plotting the natural logarithm of the HF concentration vs. the natural logarithm of the elapsed time from the HF maximum, as seen in Figure 5. As the HF concentration for tests with FE-36 plus 15% APP were well below the target concentration of 500 ppm, no further analysis of the data was warranted, as well as the fact that the discharged APP concentration probably exceeded acceptable respiratory exposure levels [16]. Figure 5, being on a ln-ln scale, indicates that the dissipation of HF vs. time is a second-order decay process. Results from linear regression analysis of the data in Figure 5 are presented in Table 3.
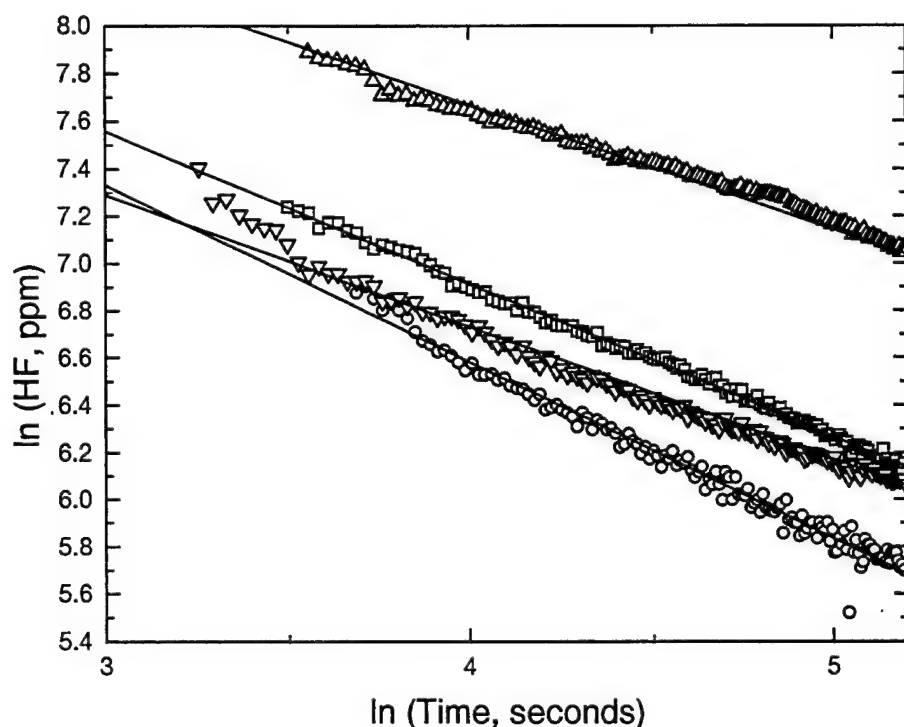
**Figure 5. Rate Plot of ln (HF) Concentrations vs. ln (Time) for Fires Extinguished by FE-36 Only (□), FE-36 Plus 7% APP (O), FM-200 (△), and FM-200 Plus 15% APP (▽). The Straight Solid Lines Represent Linear Regression Analysis of the Data.**

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Table 3. Slope Values From Linear Regression Analysis of HF Dissipation Rates

	FE-36	FE-36 Plus 7% APP	FM-200	FM-200 Plus 15% APP
Slopes (ppm/s)	−0.65	−0.75	−0.52	−0.55

The difference in slopes for between FE-36 and FE-36 plus 7% APP tests is approximately 13% greater for the fires extinguished by FE-36 plus 7% APP, while the difference between the FM-200 and FM-200 plus 15% APP is approximately 5%. Thus, the faster decreases in HF concentrations from fires extinguished by FE-36 plus APP and FM-200 plus APP vs. FE-36 and FM-200, respectively, is attributed to the presence of APP.

The primary concern with combining a powder substance like APP in a hand-held extinguisher with the fluorinated agents is that, when the extinguisher contents are released, the powder is temporally suspended in the air, forming a visibly dense "cloud" that could be difficult to see through. To address and quantify this situation, a series of obscuration measurements was conducted. Figure 6 presents results from the obscuration measurements with temporally resolved percent transmission profiles measured during and following the release of the FE-36 plus APP and the $NaHCO_3$ plus N_2 extinguishers inside an M1-Abrams combat vehicle. The profiles indicate that the maximum light attenuations were 0% transmission for the $NaHCO_3$ plus N_2 extinguisher and 18% transmission for the FE-36 plus APP extinguisher. Empirical correlations using a VHS video taken inside the vehicle during the extinguishers discharge indicate that clear visibility to the human eye correlates to an attenuation level of approximately 70% transmission. Thus, all percent transmission levels recorded below 70% correspond to an obscured field of view at a distance of 30.48 cm. The time duration that visibility is less than 70% transmission for the $NaHCO_3$ extinguisher is 63 s, while the FE-36 plus APP extinguisher experiences less than 70% transmission for 49 s. The more rapid return to visibility (i.e., ≥70% transmission) using the FE-36 plus APP extinguisher is attributed to the fact that the powder is not released in a dry state, but, rather, it is "wet" and thus falls faster to the vehicle floor.
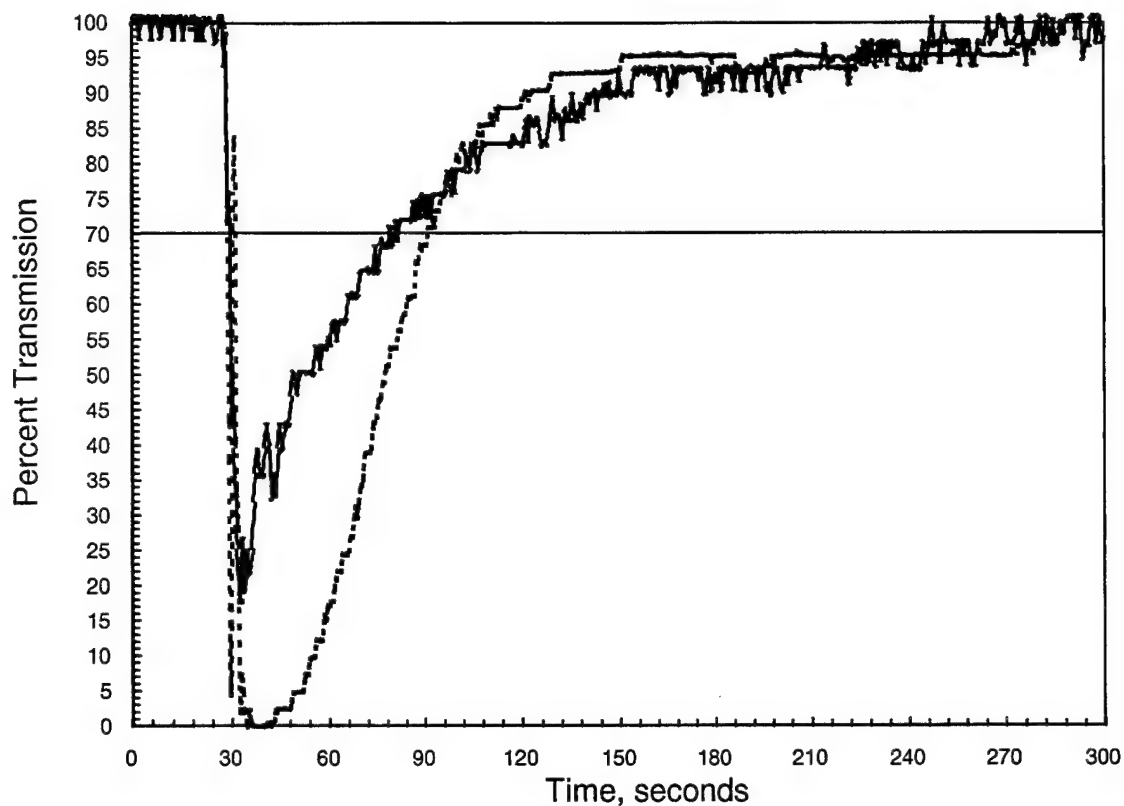
Figure 6. Percent Transmission Profiles Collected From Measurement of Light Attenuation While an Extinguisher Containing Either FE-36 Plus APP (Solid Line) or FE-36 Plus NaHCO$_3$ (Dashed Line) Was Released Inside an M1 Combat Vehicle. The Horizontal Line Drawn Across the Graph Is the 70% Transmission Level That Corresponds to the Minimal Level of Clear Visibility to the Human Eye.

4. Conclusions

NIR-TDLAS has been demonstrated to measure HF in a practical field application. The results presented here indicate that HF concentrations produced from fires extinguished by FE-36 plus APP and FM-200 plus APP are being reduced in the cubic test container and that the presence of APP accelerates this reduction. Thus the combination of APP in an extinguisher containing FE-36 or FM-200 appears to reduce HF levels. Visibility reduction during extinguisher deployment was measured inside an actual combat vehicle for extinguishers

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containing FE-36 plus APP and NaHCO₃ plus N_2. From an experimental standpoint, more tests should probably be conducted to analyze the reacted APP to understand how APP reacts with HF. Future tests will attempt to meet this concern in order to develop a chemical kinetic mechanism for post-fire HF activity.

5. References

1. McNesby, K. L., R. G. Daniel, J. M. Widder, and A. W. Miziolek. "Spectroscopic Investigation of Atmospheric-Pressure Counterflow Diffusion Flames Inhibited by Halons." *Applied Spectroscopy*, vol. 50, p. 126, 1996.

2. McNesby, K. L., R. R. Skaggs, A. W. Miziolek, M. Clay, S. Hoke, and C. S. Miser. "Diode Laser-Based Measurements of Hydrogen Fluoride Gas During Chemical Suppression of Fires." *Applied Physics B*, vol. 67, p. 443, 1998.

3. Hanson, R. K. "High Resolution Spectroscopy of Combustion Gases Using a Tunable IR Diode Laser." *Applied Optics,* vol. 19, p. 482, 1980.

4. Varghese, P. L., and R. K. Hanson. "Tunable Infrared Diode Laser Measurements of Line Strengths and Collision Widths of $^{12}C^{16}O$ at Room Temperature." *Journal of Quantitative Spectroscopy and Radiative Transfer*, vol. 24, p. 479, 1980.

5. Schoenung, S. M., and R. K. Hanson. "Laser Absorption Sampling Probes for Temporally and Spatially Resolved Combustion Measurements." *Combustion Science and Technology*, vol. 24, p. 227, 1981.

6. Miller, J. H., S. Elreedy, B. Ahvazi, F. Woldu, and P. Hassanzadeh. "Tunable Diode Laser Measurements of Carbon Monoxide Concentrations and Temperatures in a Methane Air Laminar Diffusion Flame." *Applied Optics*, vol. 32, p. 6082, 1993.

7. Nguyen, Q. V., B. L. Edgar, R. W. Dibble, and A. Gulati. "Experimental and Numerical Comparison of Extractive and In Situ Laser Measurements of Non-Equilibrium Carbon Monoxide in Lean-Premixed Natural Gas Combustion." *Combustion and Flame*, vol. 100, p. 395, 1995.

8. Skaggs, R. R., and J. H. Miller. "A Study of Carbon Monoxide in a Series of Laminar Ethylene/Air Diffusion Flames Using Tunable Diode Laser Absorption Spectroscopy." *Combustion and Flame*, vol. 100, p. 430, 1995.

9. Skaggs, R. R., and J. H. Miller. "Tunable Diode Laser Absorption Measurements of Carbon Monoxide and Temperature in a Time-Varying, Methane/Air, Non-Premixed Flame." *Twenty-Sixth (International) Symposium on Combustion*, The Combustion Institute, Pittsburgh, p.1181, 1996.

10. Reid, J., and D. Labrie. "Second Harmonic Detection With Tunable Diode Lasers -- Comparison of Experiment and Theory." *Applied Physics B*, vol. 26, p. 203, 1981.

11. Cassidy, D. T., and J. Reid. "Atmospheric Pressure Monitoring of Trace Gases Using Tunable Diode Lasers." *Applied Optics*, vol. 21, p. 1186, 1982.

12. Bruce, D. M., and D. T. Cassidy. "Detection of Oxygen Using Short External Cavity GaAs Semiconductor Diode Lasers." *Applied Optics*, vol. 29, p. 1327, 1990.

13. Silver, J. A., D. S. Bomse, and A. C. Stanton. "Diode Laser Measurements of Trace Gase Concentrations of Ammonia in an Entrained-Flow Coal Reactor." *Applied Optics*, vol. 30, p. 1505, 1991.

14. Bomse, D. S., A. C. Stanton, and J. A. Silver. "Frequency Modulation and Wavelength Modulation Spectroscopies: Comparison of Experimental Methods Using a Lead Salt Diode Laser." *Applied Optics,* vol. 31, p. 718, 1992.

15. Skaggs, R. R., R. G. Daniel, A. W. Miziolek, K. L. McNesby, C. Herud, W. Bolt, and D. Horton. "Diode Laser Measurements of HF Concentrations From Heptane/Air Pan Fires Extinguished by FE-36 And FE-36 Plus Ammonium Polyphosphate." *Proceedings of the SPIE Fall Meeting: Photonics East Environmental and Industrial Monitors*, p. 156, 1998.

16. Stewart, H. Private Communication. POWSUS, Inc., 1998.

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ABERDEEN PROVING GROUND

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Diode Laser Measurements of HF Concentrations Produced From Heptane/Air Pan Fires Extinguished by FE-36, FM-200, FE-36 Plus APP, and FM-200 Plus APP

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13. ABSTRACT (Maximum 200 words)

Tunable diode laser absorption spectroscopy (TDLAS) is used to measure the time evolution of hydrogen fluoride (HF) concentrations produced from a series of enclosed heptane/air pan fires extinguished by FE-36, FM-200, FE-36 plus ammonium polyphosphate (APP), and FM-200 plus APP. For the fires studied, the change in HF gas concentration with time is dependent upon the fire-fighting chemical used to extinguish the fire. The presence of APP is observed to reduce HF concentrations in the fire enclosure. Visible attenuation spectroscopy is also used to measure the amount of light attenuation (obscuration) that occurs as a hand-held fire extinguisher containing powder fire-fighting agent is released in the crew space of an M1-Abrams land combat vehicle.

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diode laser, fire FE-36, FM-200, HF, APP

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